

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



10/537385



(43) International Publication Date  
22 July 2004 (22.07.2004)

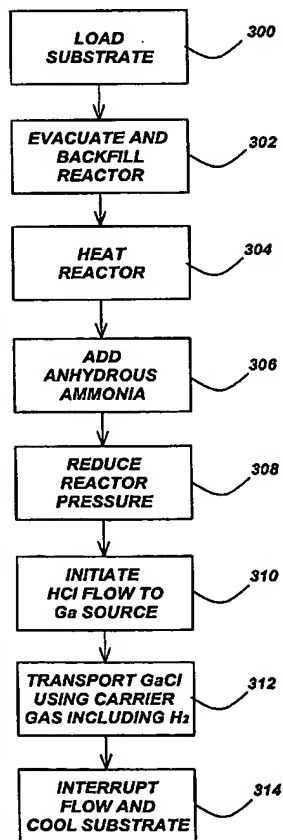
PCT

(10) International Publication Number  
WO 2004/061969 A1

- (51) International Patent Classification<sup>7</sup>: H01L 29/22, 51/40
- (21) International Application Number: PCT/US2003/021916
- (22) International Filing Date: 15 July 2003 (15.07.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
60/433,844 16 December 2002 (16.12.2002) US  
60/433,843 16 December 2002 (16.12.2002) US
- (71) Applicant (for all designated States except US): THE REGENTS OF UNIVERSITY OF CALIFORNIA [US/US]; 1111 Franklin Street, 12th Floor, Oakland, CA 94607 (US).
- (72) Inventors; and  
(75) Inventors/Applicants (for US only): HASKELL, Benjamin, A. [US/US]; 724 Kroeber Walk, #207, Goleta, CA 93117 (US). FINI, Paul, T. [US/US]; 218 West Mason Street, Santa Barbara, CA 93101 (US). MATSUDA, Shigemasa [JP/JP]; 3-19-1-212 Hyakunin-cho, Shinjuku-ku, Tokyo 169-0073 (JP). CRAVEN, Michael, D. [US/US]; 68 1/2 Deerhurst Drive, Goleta, CA 93117 (US). DENBAARS, Steven, P. [US/US]; 287 King Daniel Lane, Goleta, CA 93117 (US). SPECK, Jame, S. [US/US]; 947 West Campus Lane, Goleta, CA 93117 (US). NAKAMURA, Shuji [JP/US]; 4517 Vieja Drive, Santa Barbara, CA 93110 (US).
- (74) Agent: GATES, George, H.; Gates & Cooper LLP, 6701 Center Drive West, Suite 1050, Los Angeles, CA 90045 (US).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,

[Continued on next page]

(54) Title: GROWTH OF PLANAR, NON-POLAR A-PLANE GALLIUM NITRIDE BY HYDRIDE VAPOR PHASE EPITAXY



(57) Abstract: Highly planar non-polar a-plane GaN films are grown by hydride vapor phase epitaxy (HVPE). The resulting films are suitable for subsequent device regrowth by a variety of growth techniques

WO 2004/061969 A1



GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Declaration under Rule 4.17:**

— *of inventorship (Rule 4.17(iv)) for US only*

**Published:**

— *with international search report*

(84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

GROWTH OF PLANAR, NON-POLAR A-PLANE GALLIUM NITRIDE BY  
HYDRIDE VAPOR PHASE EPITAXY

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to the following co-pending and commonly-assigned United States Provisional Patent Applications:

Serial No. 60/433,844, entitled "TECHNIQUE FOR THE GROWTH OF  
5 PLANAR, NON-POLAR A-PLANE GALLIUM NITRIDE BY HYDRIDE VAPOR  
PHASE EPITAXY," filed on December 16, 2002, by Benjamin A. Haskell, Paul T.  
Fini, Shigemasa Matsuda, Michael D. Craven, Steven P. DenBaars, James S. Speck,  
and Shuji Nakamura, attorneys docket number 30794.94-US-P1; and

Serial No. 60/433,843, entitled "GROWTH OF REDUCED DISLOCATION  
10 DENSITY NON-POLAR GALLIUM NITRIDE BY HYDRIDE VAPOR PHASE  
EPITAXY," filed on December 16, 2002, by Benjamin A. Haskell, Michael D.  
Craven, Paul T. Fini, Steven P. DenBaars, James S. Speck, and Shuji Nakamura,  
attorneys docket number 30794.93-US-P1;

both of which applications are incorporated by reference herein.

15 This application is related to co-pending and commonly-assigned International  
Application No. PCT/US03/-----, entitled "GROWTH OF REDUCED  
DISLOCATION DENSITY NON-POLAR GALLIUM NITRIDE BY HYDRIDE  
VAPOR PHASE EPITAXY," filed on same date herewith, by Benjamin A. Haskell,  
Michael D. Craven, Paul T. Fini, Steven P. DenBaars, James S. Speck, and Shuji  
20 Nakamura, attorneys docket number 30794.93-WO-U1; which application claims  
priority to the co-pending and commonly-assigned United States Provisional Patent  
Application Serial No. 60/433,843, entitled "GROWTH OF REDUCED  
DISLOCATION DENSITY NON-POLAR GALLIUM NITRIDE BY HYDRIDE  
VAPOR PHASE EPITAXY," filed on December 16, 2002, by Benjamin A. Haskell,  
25 Michael D. Craven, Paul T. Fini, Steven P. DenBaars, James S. Speck, and Shuji  
Nakamura, attorneys docket number 30794.93-US-P1; and United States Provisional

Application Serial No. 60/433,844, entitled "TECHNIQUE FOR THE GROWTH OF PLANAR, NON-POLAR A-PLANE GALLIUM NITRIDE BY HYDRIDE VAPOR PHASE EPITAXY," filed on December 16, 2002, by Benjamin A. Haskell, Paul T. Fini, Shigemasa Matsuda, Michael D. Craven, Steven P. DenBaars, James S. Speck, and Shuji Nakamura, attorneys docket number 30794.94-US-P1; which applications are incorporated by reference herein.

1. Field of the Invention.

The invention is related to semiconductor materials, methods, and devices, and more particularly, to the growth of planar, non-polar, a-plane gallium nitride (GaN) by hydride vapor phase epitaxy (HVPE).

2. Description of the Related Art.

(Note: This application references a number of different patents, applications and/or publications as indicated throughout the specification by one or more reference numbers. A list of these different publications ordered according to these reference numbers can be found below in the section entitled "References." Each of these publications is incorporated by reference herein.)

The usefulness of gallium nitride (GaN) and its ternary and quaternary compounds incorporating aluminum and indium (AlGaN, InGaN, AlInGaN) has been well established for fabrication of visible and ultraviolet optoelectronic devices and high-power electronic devices. (See References 1-3.) These devices are typically grown epitaxially by growth techniques including molecular beam epitaxy (MBE), metalorganic chemical vapor deposition (MOCVD), or hydride vapor phase epitaxy (HVPE).

GaN and its alloys are most stable in the hexagonal wurtzite crystal structure, in which the crystal is described by two (or three) equivalent basal plane axes that are rotated 120° with respect to each other (the a-axes), all of which are perpendicular to a unique c-axis. FIG. 1 is a schematic of a generic hexagonal wurtzite crystal structure

100 and planes of interest 102, 104, 106, 108 with these axes 110, 112, 114, 116 identified therein.

As a consequence of the gallium and nitrogen atom positions within the würtzite structure, as one proceeds from plane to plane along the c-axis, each plane  
5 will contain only one type of atoms, either Ga or N. In order to maintain charge neutrality, GaN crystals terminate with one c-face that contains only nitrogen atoms (the N-face), and one c-face that only contains gallium atoms (the Ga-face). As a consequence, GaN crystals are polarized along the c-axis. The spontaneous polarization of these crystals is a bulk property and depends on the structure and  
10 composition of the crystal.

Due to the relative ease of growing planar Ga-face c-planes, virtually all GaN-based devices are grown parallel to the polar c-axis. Furthermore, strain at interfaces between adjacent dissimilar layers gives rise to piezoelectric polarization. The total polarization is a sum of the spontaneous and piezoelectric contributions, the net effect  
15 of which causes charge separation within quantum heterostructures. Charge separation within quantum wells decreases the electron-hole recombination efficiency and red-shifts the emission wavelength [4-8], both of which are undesirable in the operation of the operation of light-emitting optoelectronic devices. It is believed that the efficiency of GaN light emitting devices would be enhanced were it possible to eliminate the  
20 polarization effects inherent to c-axis oriented devices.

One possible approach to eliminating the piezoelectric polarization effects in GaN optoelectronic devices is to grow the devices on non-polar planes of the crystal. (See References 9-11.) Such planes contain equal numbers of Ga and N atoms and are charge-neutral. Furthermore, subsequent non-polar layers are equivalent to one  
25 another so the bulk crystal will not be polarized along the growth direction. One such family of symmetry-equivalent non-polar planes in GaN is the  $\{11\bar{2}0\}$  family, known collectively as a-planes. Growth on electronic devices, such as high electron mobility transistors; or optoelectronic devices, such as visible and ultraviolet laser diodes and

light-emitting diodes; on a-plane substrates could yield significantly enhanced device performance compared to equivalent devices grown on c-plane GaN.

Bulk crystals of GaN are not available so it is not possible to simply cut a crystal to present a surface for subsequent device regrowth. Commonly, GaN films  
5 are initially grown heteroepitaxially, i.e. on foreign substrates that provide a reasonable lattice match to GaN. In recent years, a number of research groups have found it possible to utilize HVPE as a means of heteroepitaxially depositing GaN films that are thick enough ( $>200\text{ }\mu\text{m}$ ) to remove the foreign substrate, yielding a free-  
standing GaN substrate that may then be used for homoepitaxial device regrowth.  
10 (See References 12-13.) HVPE has the advantage of growth rates that are one to two orders of magnitude greater than that of MOCVD and as many as three orders of magnitude greater than MBE, which is an advantage that makes it attractive for substrate fabrication.

However, to date, it has only been possible to grow planar c-plane GaN films  
15 by HVPE. In the case of a-plane GaN, films grown by virtually every technique exhibit a "sawtooth" or highly faceted morphology (see References 13-15), such as is shown in FIG. 2, which is a cross-sectional scanning electron micrograph (SEM) image of a conventionally-grown a-plane GaN film. Such a surface structure is clearly unacceptable for use as either a substrate or device layer material.

20 Thus, there is a need in the art for methods of growing high-quality thick films of a-plane GaN suitable for use as substrates in homoepitaxial device layer regrowth. More specifically, there is a need in the art for methods of growing highly planar, specular a-plane GaN films. The present invention satisfies this need.

25

#### SUMMARY OF THE INVENTION

The present invention discloses a method for forming a planar, non-polar, a-plane gallium nitride (GaN) film on a substrate, comprising: (a) loading a substrate into a reactor; (b) evacuating the reactor and backfilling the reactor with purified nitrogen ( $\text{N}_2$ ) gas to reduce oxygen levels therein; (c) heating the reactor to a growth.

temperature of approximately 1040°C, with a mixture of hydrogen (H<sub>2</sub>) and nitrogen (N<sub>2</sub>) flowing through all channels in the reactor; (d) nitridating the substrate by adding anhydrous ammonia (NH<sub>3</sub>) to a gas stream in the reactor to nitridate the substrate; (e) reducing the reactor's pressure to a desired deposition pressure, wherein the desired  
5 deposition pressure is approximately 76 Torr; (f) initiating a gaseous hydrogen chloride (HCl) flow to a gallium (Ga) source to begin growth of the a-plane GaN film directly on the substrate, wherein the gaseous HCl reacts with the Ga at a temperature in excess of 600°C to form gallium monochloride (GaCl); (g) transporting the GaCl to the substrate using a carrier gas that includes at least a fraction of hydrogen (H<sub>2</sub>),  
10 wherein the GaCl reacts with ammonia (NH<sub>3</sub>) at the substrate to form the GaN film; and (h) after a desired growth time has elapsed, interrupting the gaseous HCl flow, returning the reactor's pressure to atmospheric pressure, reducing the reactor's temperature to room temperature, and including anhydrous ammonia (NH<sub>3</sub>) in a gas stream to prevent decomposition of the GaN film during the reduction of the reactor's  
15 temperature.

### BRIEF DESCRIPTION OF THE DRAWINGS

Referring now to the drawings in which like reference numbers represent corresponding parts throughout:

20 FIG. 1 is a schematic of a generic hexagonal structure and planes of interest with these axes identified therein;

FIG. 2 is a cross-sectional scanning electron micrograph (SEM) image of a conventionally-grown a-plane GaN film exhibiting a sawtooth morphology;

FIG. 3 is a flowchart that illustrates the steps of the process according to the preferred embodiment of the present invention; and  
25

FIG. 4 is a cross-sectional scanning electron micrograph (SEM) image of an a-plane gallium nitride film grown using the techniques described by the present invention.

FIG. 5(a) shows an optical contrast micrograph of a representative a-plane GaN film grown by hydride vapor phase epitaxy (HVPE);

FIG. 5(b) shows a cross-sectional scanning electron (SEM) micrograph of sub-surface, internal cracks;

5        FIG. 6 shows a representative atomic force micrograph (AFM) from an a-plane GaN film; and

FIGS. 7(a) and (b) show plan-view transmission electron micrographs (TEMs) of an a-plane GaN film.

## 10                    DETAILED DESCRIPTION OF THE INVENTION

In the following description of the preferred embodiment, reference is made to the accompanying drawings which form a part hereof, and in which is shown by way of illustration a specific embodiment in which the invention may be practiced. It is to be understood that other embodiments may be utilized and structural changes may be  
15        made without departing from the scope of the present invention.

### Overview

The present invention uses hydride vapor phase epitaxy (HVPE) to grow planar, non-polar, a-plane gallium nitride (GaN) films. Specifically, the present  
20        invention relies on the use of a combination of several growth parameters to achieve these planar, non-polar, a-plane gallium nitride (GaN) films:

1.        The use of a suitable substrate, such as, but not limited to, an r-plane sapphire ( $\text{Al}_2\text{O}_3$ ) substrate.
2.        The use of a fraction of hydrogen ( $\text{H}_2$ ) as a carrier gas for the final  
25        growth stage in one or more of the gas streams in a reactor.
3.        A reduced reactor pressure, below atmospheric pressure (760 Torr), for the film deposition step.



### Process Steps

FIG. 3 is a flowchart that illustrates the steps of the process according to the preferred embodiment of the present invention. These steps comprise a typical growth sequence that yields high-quality, planar, non-polar, a-plane GaN films using  
5 a conventional three-zone horizontal directed-flow HVPE system.

Block 300 represents the step of loading a substrate into a reactor without any ex situ cleaning. In the preferred embodiment, the substrate is an r-plane  $\{1\bar{1}02\}$  sapphire ( $\text{Al}_2\text{O}_3$ ) substrate, although other materials, such as silicon carbide ( $\text{SiC}$ ), may be used as well.

10 Block 302 represents the step of evacuating the reactor and backfilling the reactor with purified nitrogen ( $\text{N}_2$ ) gas to reduce oxygen and water vapor levels therein, before heating the reactor. This step is typically repeated to further reduce the oxygen and water vapor presence in the system.

Block 304 represents the step of heating the reactor to a growth temperature of  
15 approximately  $1040^\circ\text{C}$ , with a mixture of  $\text{H}_2$  and  $\text{N}_2$  flowing through all channels in the system.

Block 306 represents the step of nitridating the sapphire substrate, once the reactor reaches the growth temperature, wherein the nitridating step comprises adding anhydrous ammonia ( $\text{NH}_3$ ) to a gas stream in the reactor to nitridate the surface of the  
20 sapphire substrate. The step of nitridating the substrate is performed at a temperature in excess of  $900^\circ\text{C}$ .

Block 308 represents the step of reducing the reactor's pressure to a desired deposition pressure. In the preferred embodiment, the desired deposition pressure is below atmospheric pressure (760 Torr), and more specifically, the desired deposition  
25 pressure ranges from 5 to 100 Torr. In embodiment, the desired deposition pressure is approximately 76 Torr.

Block 310 represents the step of initiating a gaseous hydrogen chloride ( $\text{HCl}$ ) flow to a gallium ( $\text{Ga}$ ) source to begin growth of the a-plane GaN film directly on the sapphire substrate without the use of any low-temperature buffer or nucleation layers. ...

Conventional metal source HVPE involves an in situ reaction of a halide compound, such as (but not limited) to, gaseous HCl with the metallic Ga at a temperature in excess of 600°C to form a metal halide species, such as gallium monochloride (GaCl).

Block 312 represents the step of transporting the GaCl to the substrate by a carrier gas that includes at least a fraction of hydrogen (H<sub>2</sub>) in one or more of the gas streams in the reactor. The carrier gas may also include nitrogen, helium, or argon. Either in transport to the substrate, at the substrate, or in an exhaust stream, the GaCl reacts with the NH<sub>3</sub> to form the GaN film. Reactions that occur at the substrate have the potential to yield the GaN film on the substrate, thereby resulting in crystal growth. Typical V/III ratios (the molar ratio of NH<sub>3</sub> to GaCl) are 1-50 for this process. Note that the NH<sub>3</sub>/HCl ratio need not equal the V/III ratio due to supplemental HCl injection downstream of the Ga source or incomplete reaction of HCl with the Ga source.

Block 314 represents, after a desired growth time has elapsed, the step of interrupting the gaseous HCl flow, returning the reactor pressure, and reducing the reactor's temperature to room temperature. The interrupting step further comprises including NH<sub>3</sub> in a gas stream to prevent decomposition of the GaN film during the reduction of the reactor's temperature. The reactor pressure may be reduced to atmospheric pressure or lower, e.g., wherein the cooling is performed between 5 and 760 Torr.

Typical growth rates for the GaN film range from 1 to 50 μm per hour by this process. These growth rates are dependent on a number of growth parameters, including, but not limited to, the source and substrate temperatures, flow rates of the various gases into the system, the reactor geometry, etc., and can be varied over reasonably wide ranges while still yielding planar a-plane GaN films. The preferred values for most of these parameters will be specific to the growth reactor geometry.

The reference in the process steps above to the "final growth stage" refers to the observation that it is possible to planarize otherwise rough or sawtoothed films by concluding the growth stage with a step of suitable duration using the above-described.

conditions. The earlier stages of growth may incorporate any growth parameters that yield nominally a-plane oriented material, regardless of film morphology.

Preferably, the above process steps create a planar, non-polar, a-plane gallium nitride (GaN) film. Moreover, devices manufactured using this method include laser  
5 diodes, light-emitting diodes and transistors.

### Experimental Results

In experiments by the inventors, the above process consistently yields specular, planar a-plane GaN films. FIG. 4 is a cross-sectional SEM image of an a-  
10 plane GaN film grown using the techniques described by the present invention. Note the highly planar upper free surface shown in FIG. 4. (Note also that the striated cross-section surface is an artifact of cleaving.)

FIG. 5(a) shows a Nomarski™ optical contrast micrograph of a representative a-plane GaN film grown by HVPE. The  $(11\bar{2}0)$  GaN films are specular and optically  
15 transparent, with little detail of the surface being apparent in conventional transmission or reflection optical microscopy. The surface is characterized by long-range 'flow' patterns that have peak-to-valley heights on the order of 500 nm over 75+  $\mu\text{m}$  lateral extent, as measured by profilometry. Light scattering and refractive index contrast allow observation of sub-surface cracks oriented nearly perpendicular  
20 to the GaN c-axis.

FIG. 5(b) shows a cross-sectional scanning electron (SEM) micrograph detailing two such cracks. With few exceptions, these internal cracks, which are similar to those observed in c-plane GaN films (see Reference 17), did not reach the free surface during growth. However, 50+  $\mu\text{m}$ -thick films have exhibited cracks that  
25 propagate to the surface. These cracks result from plastic relief of tensile strain that may be a consequence of grain coalescence. (See Reference 18.) The cracks subsequently heal via local lateral overgrowth to reduce surface energy.

Atomic force microscopy (AFM) was conducted on the planar a-GaN surfaces in tapping mode using a Digital Instruments D3100™ atomic force microscope. FIG.

6 shows a representative atomic force micrograph from an a-plane GaN film. Local root-mean-square (RMS) roughness over  $2 \times 2 \mu\text{m}$  sampling areas was typically  $< 0.8$  nm. The RMS roughness over larger sampling areas ( $10\text{-}20 \mu\text{m}$ ) remained below 2 nm. The surface was dominated by a high density of nanometer-scale pits that have depths of 3-7 nm. These pits likely decorated threading dislocation terminations at the free surface. The observed surface pit density generally ranged from  $2 \times 10^9$  to  $9 \times 10^9 \text{ cm}^{-2}$ . Additionally,  $\sim 1$  nm high steps oriented roughly perpendicular to the GaN c-axis were apparent in the AFM image.

Structural characteristics of the planar a-plane GaN films were evaluated by x-ray diffraction (XRD) and plan-view transmission electron microscopy (TEM). XRD was performed using Cu K $\alpha$  radiation in a Philips MRD Pro<sup>TM</sup> four-circle x-ray diffractometer operating in receiving slit mode.  $\omega$ -2 $\theta$  scans of the a-GaN films exhibited peaks that were indexed to the r-plane sapphire ( $1\bar{1}02$ ), ( $2\bar{2}04$ ), and ( $3\bar{3}06$ ) reflections, and the ( $11\bar{2}0$ ) GaN reflection. No GaN (0002) reflection was observed, demonstrating that within the detection limits of this technique, the films were uniformly a-plane-oriented.  $\omega$  rocking curves were measured on the on-axis ( $11\bar{2}0$ ) reflection for geometries in which the GaN [ $\bar{1}100$ ] and [0001] directions were in a coplanar geometry. Typical full widths at half maximum (FWHM) for the ( $11\bar{2}0$ ) reflection in these geometries were 1040-1045 arcsec. The  $30^\circ$  off-axis ( $10\bar{1}0$ ) reflection was measured by tilting the samples relative to the scattering plane (skew geometry), yielding a FWHM on the order of 3000 arcsec. The on-axis peak width was comparable to that observed for planar MOCVD-grown a-plane GaN films (see Reference 19), while the off-axis peak width was roughly twice as large, indicating a more defined cell structure and higher mosaic content in the HVPE-grown films. (See Reference 20.)

FIG. 7 shows plan-view transmission electron micrographs of an a-plane GaN film. FIG. 7(a) was imaged under the  $g = 0002$  diffraction condition, revealing threading dislocations having a Burgers vector component parallel to the GaN [0001] direction. Thus, these are edge component dislocations. The c-component dislocation

density ranged from  $9 \times 10^9 \text{ cm}^{-2}$  to  $2 \times 10^{10} \text{ cm}^{-2}$  in these samples in agreement with AFM pit density measurements and TEM of MOCVD-grown a-plane GaN films. (See Reference 19.) The TEM image in FIG. 7(b), taken under the  $g = 1\bar{1}00$  diffraction condition, shows a stacking fault density of  $\sim 4 \times 10^5 \text{ cm}^{-1}$ , again comparable with the  $3.8 \times 10^5 \text{ cm}^{-1}$  observed for planar MOCVD-grown a-plane GaN films. (See Reference 19.) These basal-plane stacking faults are likely related to the presence of exposed nitrogen-face ( $000\bar{1}$ ) surfaces during the early stages of growth. Additional imaging with varying sample tilt in the  $g = 1\bar{1}00$  diffraction condition revealed  $\sim 7 \times 10^9 \text{ cm}^{-2}$  Shockley partial dislocations having Burgers vectors  $b = \frac{1}{3}\langle 1\bar{1}00 \rangle$ .

10

### References

The following references are incorporated by reference herein:

1. T. Nishida and N. Kobayashi, Phys. Stat. Sol. (a), 188 (1), 113 (2001).
- 15 2. S. Nakamura, G. Fasol, and S. J. Pearton, The Blue Laser Diode. New York: Springer, 2000.
3. L. F. Eastman and U. K. Mishra, IEEE Spectrum, 39 (5), 28 (2002).
4. T. Takeuchi, C. Wetzel, S. Yamaguchi, H. Sakai, H. Amano, I. Akasaki, Y. Kaneko, S. Nakagawa, Y. Yamaoka, and N. Yamada, Appl. Phys. Lett. 20 73 (12) 1691 (1998).
5. I. Jin Seo, H. Kollmer, J. Off, A. Sohmer, F. Scholz, and A. Hangleiter, Phys. Rev. B, 57 (16) R9435 (1998).
6. R. Langer, J. Simon, V. Ortiz, N. T. Pelekanos, A. Barski, R. Andre, and M. Godlewski, Appl. Phys. Lett., 74 (25) 3827 (1999).
- 25 7. P. Lefebvre, J. Allegre, B. Gil, H. Mathieu, N. Grandjean, M. Leroux, J. Massies, and P. Bigenwald, Phys. Rev. B, 59 (23) 15363 (1999).
8. P. Lefebvre, A. Morel, M. Gallart, T. Taliercio, J. Allegre, B. Gil, H. Mathieu, B. Damilano, N. Grandjean, and J. Massies, Appl. Phys. Lett., 78 (9) 1252 (2001).

9. P. Waltereit, O. Brandt, A. Trampert, H. T. Grahn, J. Menniger, M. Ramsteiner, M. Reiche, and K. H. Ploog, *Nature (London)*, 406, 865 (2000).
10. M.D. Craven, P. Waltereit, F. Wu, J.S. Speck, and S.P. DenBaars, Accepted for Publication.
- 5 11. H. M. Ng, *Appl. Phys. Lett.*, 80 (23) 4369 (2002).
12. K. Motoki, T. Okahisa, N. Matsumoto, M. Matsushima, H. Kimura, H. Kasai, K. Takemoto, K. Uematsu, T. Hirano, M. Nakayama, S. Nakahata, M. Ueno, D. Hara, Y. Kumagai, A. Koukitu, and H. Seki, *Jpn. J. Appl. Phys. Part 2*, 40 (2B), L140 (2001).
- 10 13. T. Paskova, P.P. Paskov, V. Darakchieva, S. Tungasmita, J. Birch, and B. Monemar, *Phys. Stat. Sol. (a)* 183 (1) 197 (2001).
14. A. Shintani and S. Minagawa, *J. Electrochem. Soc.* 123 (10) 1575 (1976).
- 15 15. B. Monemar, O. Lagerstedt, and H. P. Gislason, *J. Appl. Phys.* 51 (1) 625 (1980).
16. M. Sano and M. Aoki, *Jpn. J. Appl. Phys.* 15 (10) 1943 (1976).
17. E. V. Etzkorn and D. R. Clarke, *J. Appl. Phys.*, 82 (2) 1025 (2001).
18. T. Böttcher, S. Einfeldt, S. Figge, R. Chierchia, H. Heinke, D. Hommel, and J. S. Speck, *Appl. Phys. Lett.*, 78 (14) 1976 (2001).
- 20 19. M. D. Craven, S. H. Lim, F. Wu, J. S. Speck, and S. P. DenBaars, *Appl. Phys. Lett.*, 81 (3) 469 (2002).
20. B. Heying, X. H. Wu, A. S. Keller, Y. Li, D. Kapolnek, B. P. Keller, S. P. DenBaars, and J. S. Speck, *Appl. Phys. Lett.*, 68, 643 (1996).

25

Conclusion

This concludes the description of the preferred embodiment of the present invention. The following describes some alternative embodiments for accomplishing the present invention.

The preferred embodiment describes a direct growth process in which the *a*-plane GaN is grown directly off of the sapphire substrate. Alternative suitable substrate materials including, but not limited to, *a*-plane silicon carbide, or particular gallate or aluminate ceramic crystals, may be used in practice of this invention.

5 HVPE growth of *c*-plane GaN is frequently carried out by using a thin GaN "template" layer that is pre-deposited on a suitable substrate by another growth technique, such as MOCVD, MBE, or HVPE. The use of templates for subsequent HVPE regrowth has been established as a viable technique for practicing the present invention.

10 The present invention can be used to manufacture free-standing *a*-plane GaN films or substrates. In some cases, it may be desirable to use such free-standing GaN films or substrates as "template" layers for the present invention.

The preferred embodiment describes an HVPE-based growth process utilizing a reaction between metallic gallium (Ga) and gaseous hydrogen chloride (GaCl) as the  
15 Group III source. Alternative Group III sources, such as but not limited to, gallium trichloride (GaCl<sub>3</sub>), or alternative reactive gases, such as but not limited to, hydrogen bromide (HBr), may be used in the practice of this invention without fundamentally altering the method.

Nucleation layers deposited at either low temperatures or at or above the  
20 growth temperature by a variety of growth techniques may also be used for subsequent regrowth by HVPE using the present invention.

Those skilled in the art may prefer to alter the carrier gas composition during heating or modify/omit the nitridation step described above. Such modifications do not fundamentally affect the practice of the present invention described herein.

25 Reactor geometry and design may affect the practice of the present invention. In general, exact flow rates of the various constituent gases have been omitted in the descriptions above because optimal flow rates are highly dependent on reactor design.

The typical growth rates used in the preferred embodiment are 1 to 50  $\mu\text{m}/\text{hour}$ . However, the inventors have demonstrated that *a*-plane GaN growth rates

in excess of 200  $\mu\text{m}/\text{hour}$  are possible. The use of growth rates outside of the preferred range does not fundamentally alter the practice of the invention.

5 The critical parameters for the practice of this invention are the growth pressure, the presence of hydrogen in the carrier gas stream, a growth temperature in the range of 800-1300°C, gas velocity over the substrate (which is again reactor-dependent) and the use of a suitable substrate. Other factors, including but not limited to V/III ratio, precise carrier gas composition, and precursor partial pressures may be varied significantly while still achieving the desired planar a-plane GaN films.

10 Finally, the processes described herein may be scaled for multiple wafer growth. Specifically, the present invention may be practiced through the growth of films on multiple wafers simultaneously.

In summary, the present invention describes the application of low-pressure growth utilizing hydrogen in the carrier gas stream to enable the growth of fully planar a-plane GaN films by HVPE. The resulting films are suitable for subsequent device regrowth by a variety of growth techniques.

15 The foregoing description of one or more embodiments of the invention has been presented for the purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed. Many modifications and variations are possible in light of the above teaching. It is intended that the scope of the invention be limited not by this detailed description, but rather by the claims  
20 appended hereto.



## WHAT IS CLAIMED IS:

1. A method for forming a planar, non-polar, a-plane gallium nitride (GaN) film on a substrate, comprising:
  - (a) loading a substrate into a reactor;
  - 5 (b) heating the reactor to a growth temperature;
  - (c) reducing the reactor's pressure to a desired deposition pressure, wherein the desired deposition pressure is below atmospheric pressure;
  - (d) initiating a gaseous hydrogen chloride (HCl) flow to a gallium (Ga) source to begin growth of the a-plane GaN film directly on the substrate, wherein the gaseous
  - 10 HCl reacts with the Ga to form gallium monochloride (GaCl);
  - (e) transporting the GaCl to the substrate using a carrier gas that includes at least a fraction of hydrogen (H<sub>2</sub>), wherein the GaCl reacts with ammonia (NH<sub>3</sub>) at the substrate to form the GaN film; and
  - (f) after a desired growth time has elapsed, interrupting the gaseous HCl flow,
  - 15 returning the reactor's pressure to atmospheric pressure, and reducing the reactor's temperature to room temperature.
2. The method of claim 1, wherein the substrate is a sapphire substrate,
- 20 3. The method of claim 1, wherein the substrate is coated with a thin film of GaN, aluminum nitride (AlN), or aluminum gallium nitride (AlGa<sub>N</sub>).
4. The method of claim 2, wherein the substrate is coated with a nucleation layer deposited either at low temperatures or at the growth temperature.
- 25 5. The method of claim 1, wherein the substrate is a free-standing GaN, aluminum nitride (AlN), or aluminum gallium nitride (AlGa<sub>N</sub>) film.

6. The method of claim 1, further comprising evacuating the reactor and backfilling the reactor with purified nitrogen ( $N_2$ ) gas to reduce oxygen and water vapor levels therein before heating the reactor.

5 7. The method of claim 1, further comprising nitridating the substrate, at a temperature in excess of  $900^\circ\text{C}$ ;

8. The method of claim 7, wherein the nitridating step comprises adding anhydrous ammonia ( $NH_3$ ) to a gas stream in the reactor to nitride the substrate.  
10

9. The method of claim 1, wherein the heating step (b) comprises heating the reactor to the growth temperature of approximately  $1040^\circ\text{C}$ , with a mixture of hydrogen ( $H_2$ ) and nitrogen ( $N_2$ ) flowing through all channels in the reactor.

15 10. The method of claim 1, wherein the gaseous  $HCl$  reacts with the Ga at a temperature in excess of  $600^\circ\text{C}$  to form the  $GaCl$ .

11. The method of claim 1, wherein the desired deposition pressure ranges from 5 to 100 Torr.  
20

12. The method of claim 1, wherein the desired deposition pressure is approximately 76 Torr.

13. The method of claim 1, wherein typical growth rates for the GaN film  
25 range from 1 to  $50\text{ }\mu\text{m}$  per hour.

14. The method of claim 1, wherein the interrupting step (f) further comprises including anhydrous ammonia ( $NH_3$ ) in a gas stream to prevent decomposition of the GaN film during the reduction of the reactor's temperature. ....

15. The method of claim 1, wherein the interrupting step (f) further comprises cooling the substrate at a reduced pressure between 5 and 760 Torr.

5 16. A device manufactured using the method of claim 1.

17. The device of claim 16, wherein the device is a laser diode, light-emitting diode or transistor.

10 18. A planar, non-polar, a-plane gallium nitride (GaN) film deposited on a substrate, wherein the GaN film is created using a process comprising:

(a) loading a substrate into a reactor;

(b) heating the reactor to a growth temperature;

15 (c) reducing the reactor's pressure to a desired deposition pressure, wherein the desired deposition pressure is below atmospheric pressure;

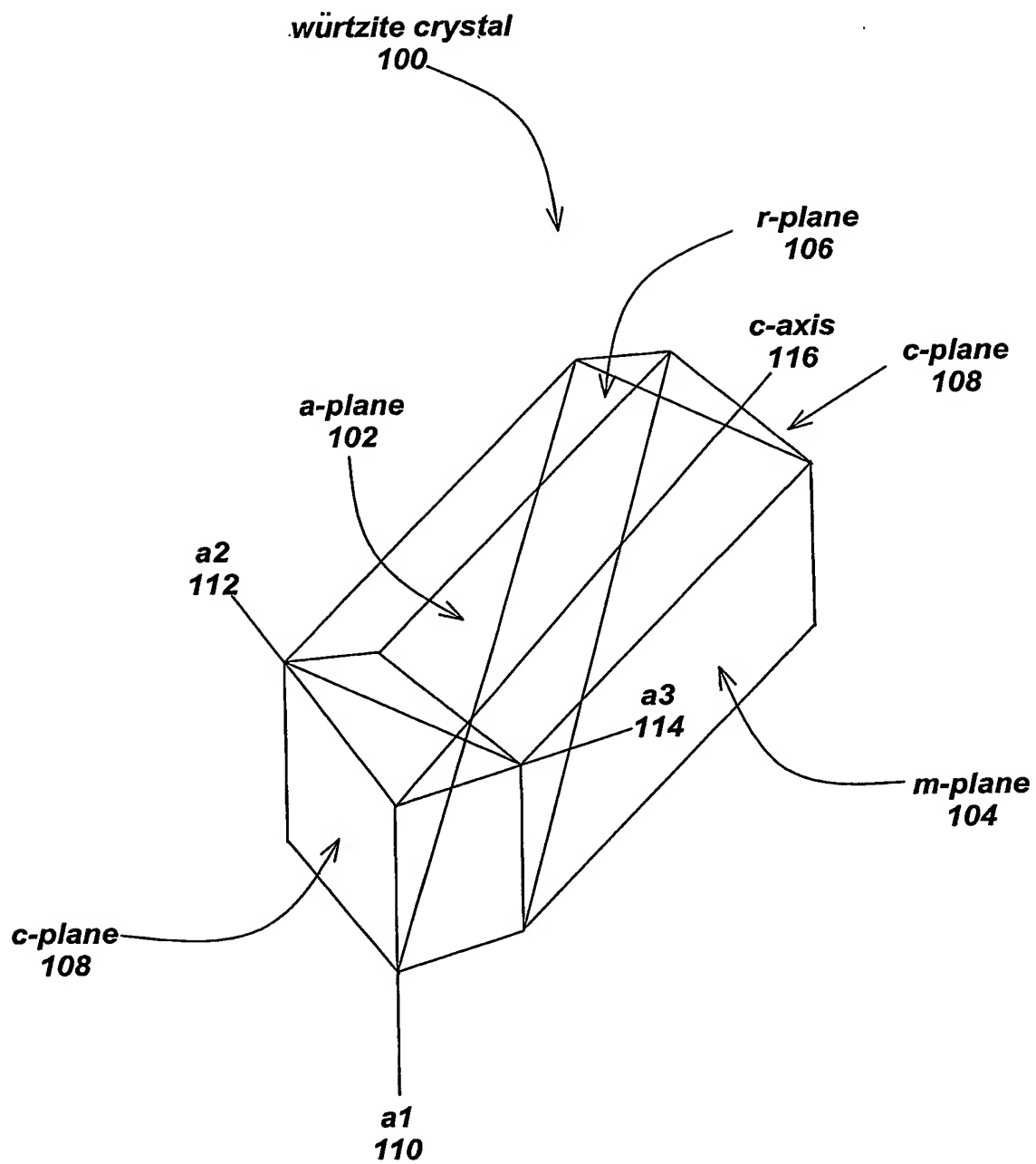
(d) initiating a gaseous hydrogen chloride (HCl) flow to a gallium (Ga) source to begin growth of the a-plane GaN film directly on the substrate, wherein the gaseous HCl reacts with the Ga to form gallium monochloride (GaCl);

20 (e) transporting the GaCl to the substrate using a carrier gas that includes at least a fraction of hydrogen (H<sub>2</sub>), wherein the GaCl reacts with ammonia (NH<sub>3</sub>) at the substrate to form the GaN film; and

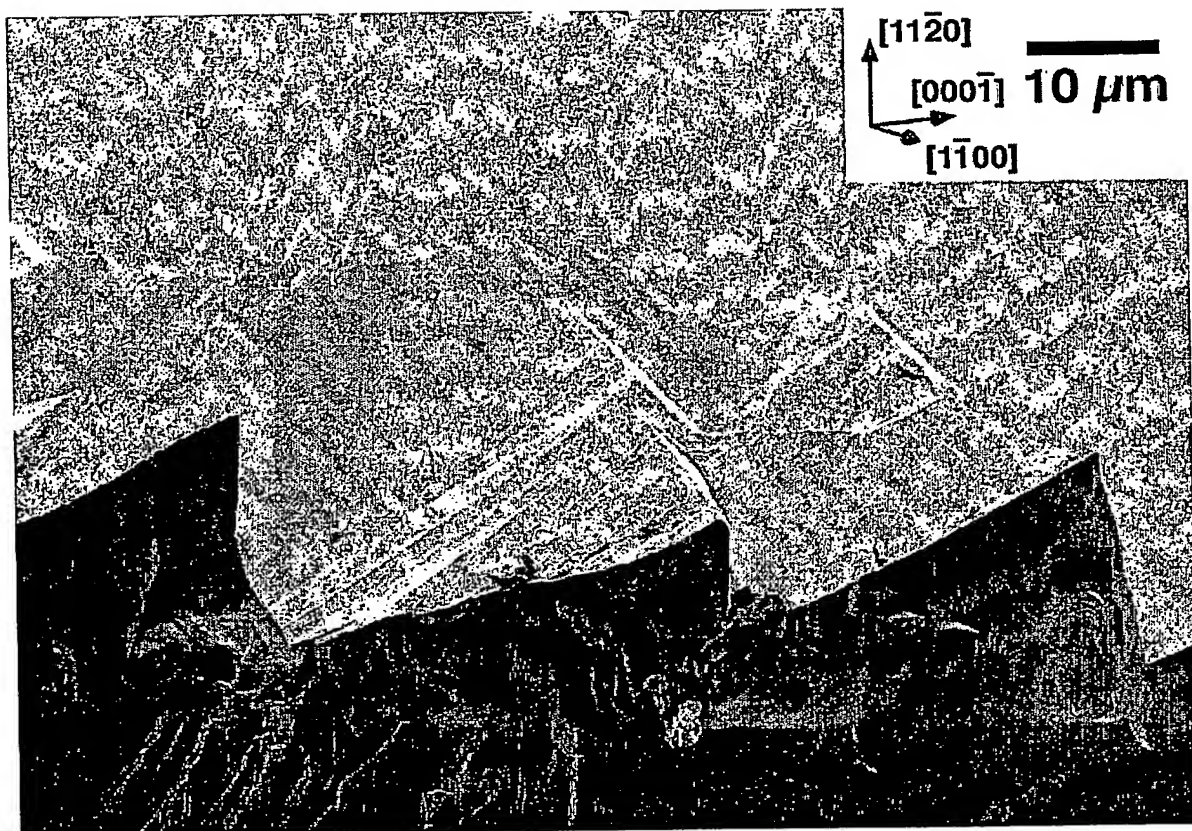
(f) after a desired growth time has elapsed, interrupting the gaseous HCl flow, returning the reactor's pressure to atmospheric pressure, and reducing the reactor's temperature to room temperature.

25

1/7

**FIG. 1**

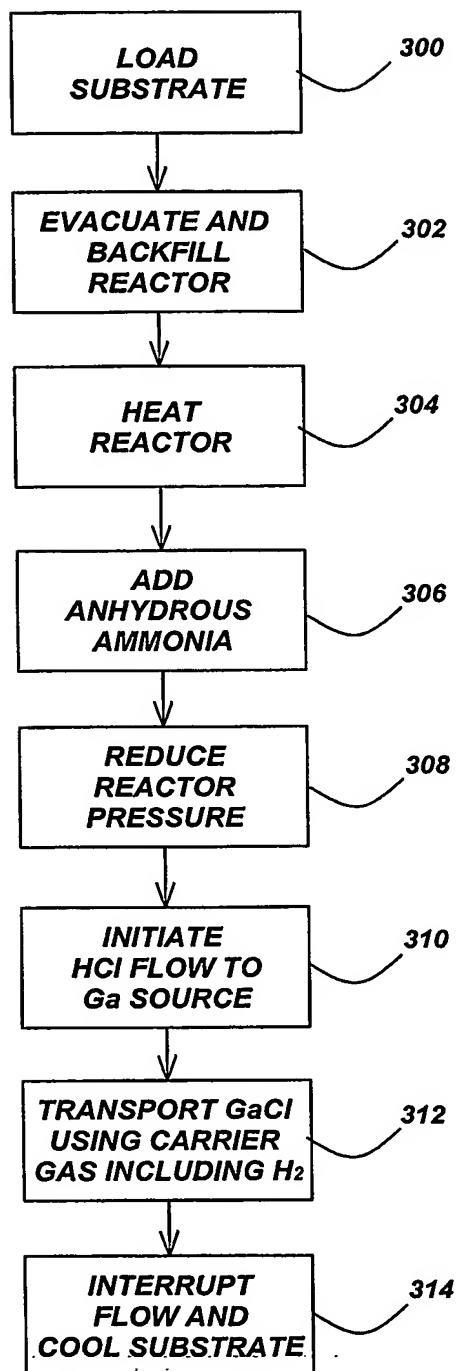
2/7

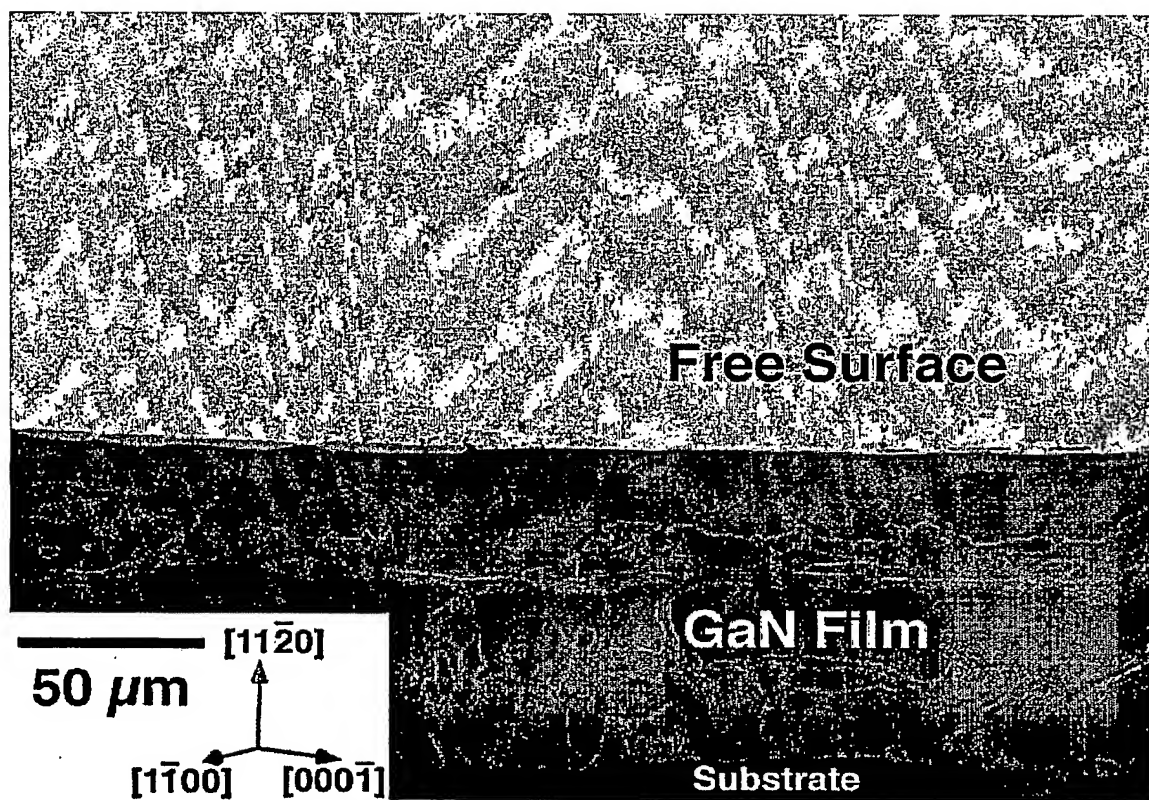


**FIG. 2**

BEST AVAILABLE COPY

3/7

**FIG. 3**

**FIG. 4**

5/7

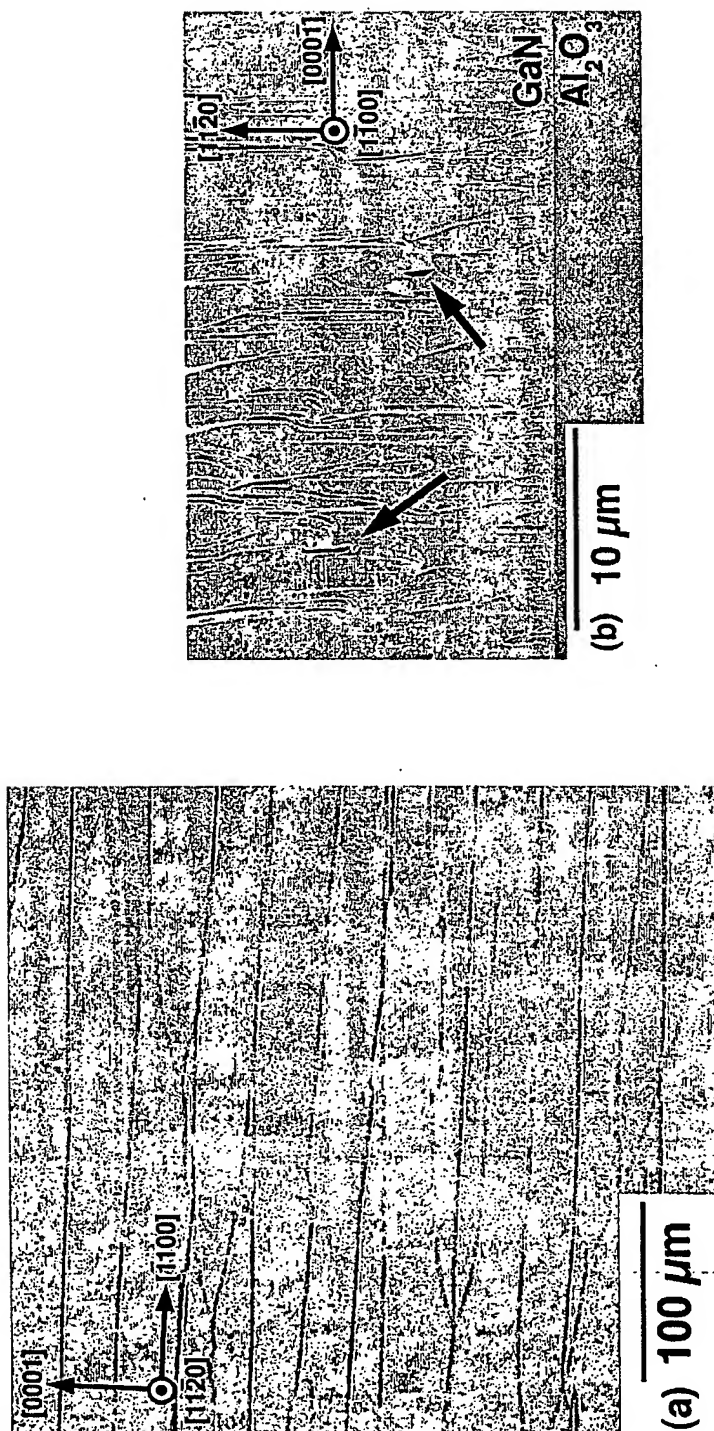
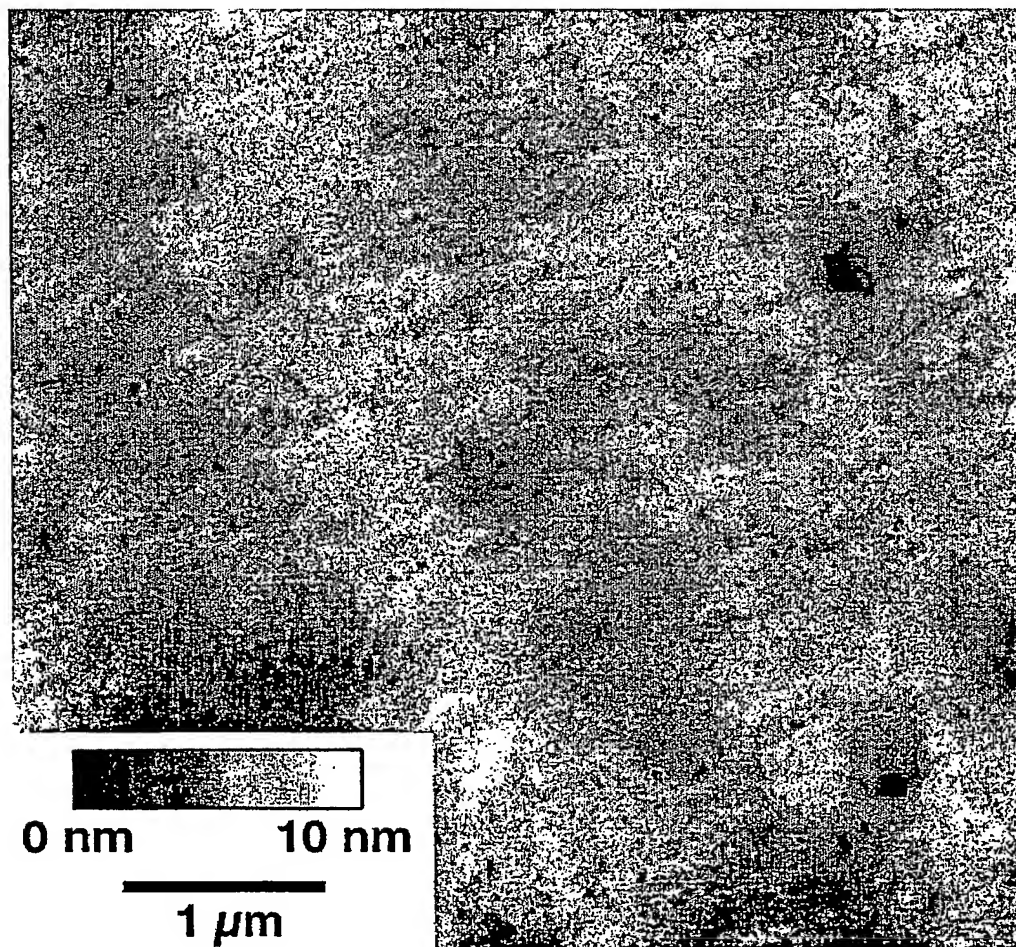


FIG. 5



6/7



**FIG. 6**

7/7

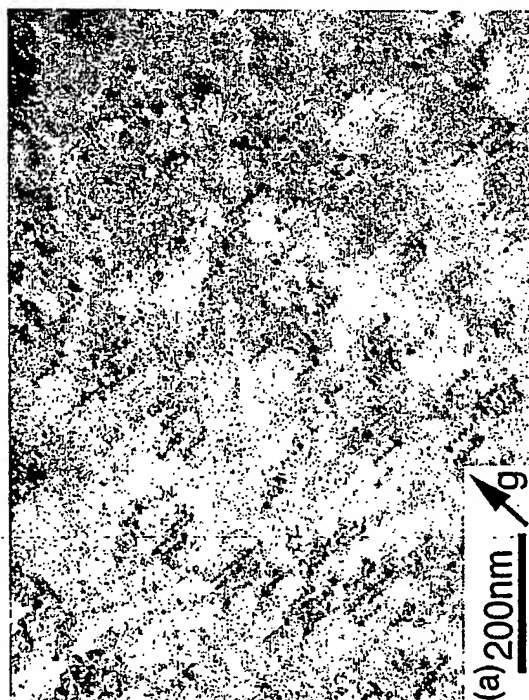
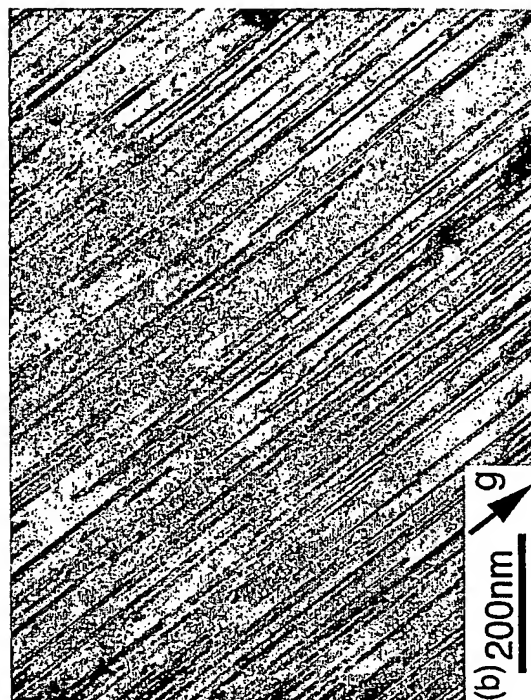


FIG. 7

BEST AVAILABLE COPY

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US03/21916

## A CLASSIFICATION OF SUBJECT MATTER

IPC(7) :H01L 29/22, 51/40

US CL :438/99; 257/614

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 438/99, 478, 930, 933,584, 602, 604, 787; 257/614, 615, 94, 103, 615, 761

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
**NONE**

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
IEEE, DWPI, EPO, JPO, IBMTDB

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6,177,292 B1 (HONG et al) 23 January 2001 (23.01.2001), see column 4, lines 33-65.	1-15
Y	US 6,180,270 B1 (COLE et al) 30 January 2001 (30.01.2001), see column 4, lines 48-65.	1-15
Y,E	US 6,635,901 B2 (SAWAKI et al) 21 October 2003 (21.10.2003), see column 5, lines 13-35.	16-18
Y	US 6,350,666 B2 (KRYLIOUK) 26 February 2002 (26.02.2002), see column 13, line 66 - column 14, lines 54.	16-18

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

16 JANUARY 2004

Date of mailing of the international search report

11 FEB 2004

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

YENNHU HUYNH

Telephone No. (703) 308-4940